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SPECIFIC FEATURES OF PRECIPITATION AND PIGMENT FORMATION IN THE Ti–Ni–Zn SYSTEM

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Based on a mixture of titanium, nickel, and zinc salts, precipitates which can serve as a "preliminary structure" in pigment formation were obtained. The precipitation conditions, composition, and properties of the precipitates are described. It is established that the Ti(IV)–Ni(II)–Zn(II) system can produce pigments of perovskite structure with good chromophore properties and resistant to the effect of glaze melts and fluxes.

A system containing a mixture of titanium (IV), nickel (II) and zinc (II) salts can serve as the basis for production of ceramic pigments with a perovskite-type structure using the precipitation method. The present paper describes the results of an experiment in obtaining precipitates which can serve as a "precursor structure" in formation of pigments with a perovskite-type structure. Precipitation was performed from aqueous 1-M solutions of titanium, nickel, and zinc sulfates. In certain cases, crystalline TiO_2 was introduced. A 1-M solution of NaOH was used as the precipitator. The quantity in each case was determined from previously plotted pH-meter curves (EV-74 universal ionometer).

According to the data obtained (Fig. 1), curves 1 and 3–5 exhibit one titration jump, and curve 2 exhibits two jumps, the second one being quite low. In order to elucidate the problem of the number of jumps corresponding to precipitation processes in the specified systems, calculations were carried out as described in [1]. The calculations revealed that titanium (when Ti(IV) is introduced to the system as a salt), zinc, and nickel hydroxides in all cases should consecutively precipitate from the solutions, and individual jumps on the curves should reflect these processes. The absence of the second and the third jumps on the curves points to the formation in alkaline precipitation of a chemical compound integrating all three ions.

In a system with the ratio of Ti(IV):Ni(II):Zn(II) = 1:0.2:0.8, all metal ions introduced in the solution prior to titration precipitated simultaneously. Since in this case the molar content of Ti(IV) is equal to the sum of the molar content of Ni(II) and Zn(II), one can assume that a titanate-like compound MeTiO_3 with $\text{Me}^{2+} = \text{Ni}^{2+}, \text{Zn}^{2+}$, and the ratio of $\text{Me}:\text{Ti} = 1:1$, was formed.

In a system with the ratio of Ti(IV):Ni(II):Zn(II) = 1:1:1, the molar content of titanium is less than the sum of

the nickel and zinc content, therefore, an excess of two-charge ions titrates with a separate jump. This gives more reason to believe that titanate is formed in the ratio of $\text{Me}:\text{Ti} = 1:1$. The excess of nickel and zinc precipitates in the form of hydroxides.

The titration curves of the systems containing Ni(II) and Zn(II) ions and solid TiO_2 likewise indicate a reaction between nickel and zinc in alkaline precipitation. A different content of TiO_2 does not affect the course of titration curves. However, difficultly soluble compounds which contain titanium dioxide in their compositions are formed in the TiO_2 –Ni(II)–Zn(II) system. If titanium is introduced in the

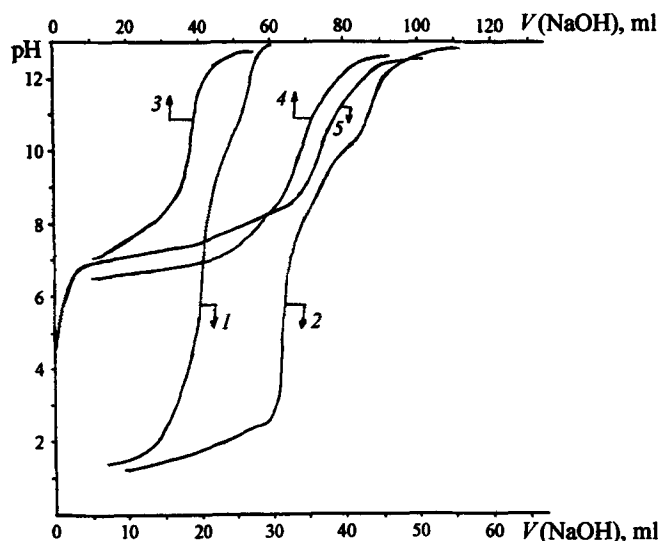


Fig. 1. Curves of potentiometric titration of solutions. 1) Ti(IV):Ni(II):Zn(II) = 1:0.2:0.8; 2) Ti(IV):Ni(II):Zn(II) = 1:1:1; 3) TiO_2 :Ni(II):Zn(II) = 1:0.8:0.2; 4) TiO_2 :Ni(II):Zn(II) = 1:1:2; 5) TiO_2 :Ni(II):Zn(II) = 1:0.8:0.4.

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ratio of $Ti:Me = 1:1$, TiO is not isolated from the system in settling. If titanium is introduced in a greater amount, the excessive TiO_2 is separated from the system in settling of the precipitate (which can be visually observed). Presumably, TiO_2 makes part of the composition of the $Ni(II) - Zn(II)$ hydroxide precipitate at the moment of its formation.

Thus, the data from pH-meter alkaline titration of the solutions of the $Ti(IV) - Ni(II) - Zn(II)$ and $TiO_2 - Ni(II) - Zn(II)$ system demonstrate the chemical interaction of the components at the moment of formation of hydroxide precipitate; moreover, with the ratio of $Ti:Me = 1:1$ typical of perovskite, individual hydroxides were not found, and with deviation from that ratio, an excess of two-charge metal ions is precipitated in the form of hydroxide.

The obtained precipitates were analyzed using the IR spectroscopy method (IR Specord-75). The absorption bands that can be distinguished in all spectra (Fig. 2) relate to stretching vibrations of the water molecules and hydroxyl group within the range of $2800 - 3700\text{ cm}^{-1}$, deformation vibrations of water molecules ($1617 - 1632\text{ cm}^{-1}$) and stretching vibrations of the $Me - O$ bond ($400 - 700\text{ cm}^{-1}$) [2]. The high intensity of these bands indicates a substantial content of nonstructural water in the precipitates [3]. The deformation vibration band of OH-groups in the range of $1047 - 1073\text{ cm}^{-1}$ [2] is not detected in the spectrum of the precipitate with a ratio of $Ti:Ni:Zn = 1:1:1$, and in the spectrum of the precipitate with a ratio of $Ti:Ni:Zn = 1:0.2:0.8$, this band is observed at 1070 cm^{-1} but its intensity is negligible.

Consequently, the hydroxide in the second case was formed as a slight impurity. This suggests that it was not hydroxides of the investigated metal ions that emerged in alkaline precipitation, but salts, namely, nickel and zinc titanates.

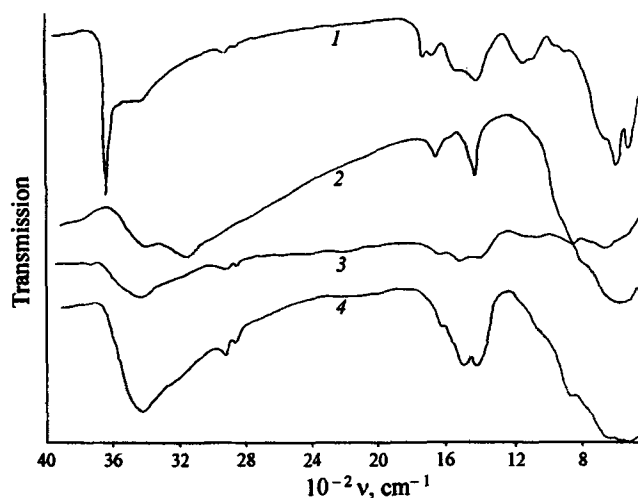


Fig. 2. IR absorption spectra of synthesized precipitates. 1) Nickel hydroxide, 2) titanium hydroxide, 3) $Ti(IV):Ni(II):Zn(II) = 1:1:1$; 4) $Ti(IV):Ni(II):Zn(II) = 1:0.2:0.8$.

The $Ti(IV) - Ni(II) - Zn(II)$ system produces precipitates which have simpler spectra than $Ni(OH)_2$. The spectra are not additive to the spectra of nickel and titanium hydroxide, which indicates the formation of new chemical compounds not containing OH-groups.

The obtained precipitates were also investigated using the method of differential thermal analysis (Table 1). The measurements were taken on a derivatograph of the Paulik – Paulik – Erdey system within the temperature range of $20 - 1000^\circ\text{C}$ at a rate of temperature increase of $10^\circ\text{C}/\text{min}$. Titanium hydroxide was subjected to stepwise dehydration: first, crystallization water was removed, then

TABLE 1

Compound	Temperature of peaks in DTA curve, $^\circ\text{C}$	Temperature interval of DTA effects, $^\circ\text{C}$	Losses		Energy effects
			wt.%, of the initial quantity	water, mole	
$TiO_2 \cdot nH_2O$	140*	40 – 240	15.7	0.83	Removal of crystallization water
	775*	510 – 820	8.6	0.42	Removal of structural water
$NiO \cdot nH_2O$	170*	75 – 270	13.8	0.66	Removal of crystallization water
	325*	270 – 570	15.6	0.77	Removal of structural water
$TiO_2 \cdot 0.8NiO \cdot 0.2ZnO \cdot nH_2O$	130*	260 – 420	13.5	1.35	Removal of crystallization water
	320*	640 – 720	10.0	0.96	Removal of structural water
	690**	20 – 260	0	0	Crystallization
	850*	720 – 1000	1.0	0.09	Removal of structural water
$TiO_2 \cdot NiO \cdot ZnO \cdot nH_2O$	140*	20 – 250	11.0	1.62	Removal of crystallization water
	350*	250 – 450	13.5	2.05	Removal of structural water
	700**	670 – 720	0	0	Crystallization
	880*	810 – 1000	1.0	0.13	Removal of structural water

* Endothermic effect.

** Exothermic effect.

structural water whose amount was half the amount of the crystallization water, and it was removed at a significantly higher temperature. A similar character of the DTA curve was observed for nickel hydroxide, but in this case, the two categories of water were comparable in quantity, and the structural water was removed at a lower temperature.

The precipitates obtained in the $\text{TiO}_2 - \text{Ni(II)} - \text{Zn(II)}$ system with different molar ratios between the components exhibit in heating three endothermic and one slight endothermic effect. At the same time, the main volume of water is removed up to the temperature of $420 - 450^\circ\text{C}$, while the water from titanium and nickel hydroxides was intensely removed up to the temperatures of 820 and 570°C , respectively. This can point to the fact that the chemical compound formed in precipitation does not belong to the hydroxide class: that is nickel-zinc titanate. The curves exhibited an exothermic effect caused by crystallization, after which the remaining structural water (1%) was removed. With an increase in the content of nickel and zinc the same effects were observed, yet they were shifted toward the region of higher temperatures.

The color parameters of the synthesized pigments were controlled by the phase composition which was analyzed on a DRON-2 unit. Solid phases represented by nickel titanate and gahnite are formed in heat treatment (1200°C). For com-

parison, we investigated a mechanical mixture of the initial powders and the precipitates obtained by the precipitation method and heat-treated as well. With an increase in the temperature, the peak intensity of the color-carrying phase of NiTiO_3 in the x-ray diffraction diagram increases (2.10 , 1.47 , 2.16 \AA), and zincate is isolated (2.59 , 1.247 , 1.61 \AA) alongside nickel titanate. Comparing the x-ray diffraction diagrams, it can be inferred that the crystal phases precipitate more intensely in the synthesis of samples using the precipitation method.

The obtained pigments have good chromophoric properties (color purity 17%, predominant wavelength 504 nm) and can be recommended for production of overglaze porcelain paints and for coloring faience glazes.

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